



# Evaluation of underwater contamination by explosives and metals at Point Amour Labrador and in the Halifax Harbour area

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**Defence R&D Canada – Valcartier**

Technical Report

DRDC Valcartier TR 2004-125

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The word "Canada" in a stylized, serif font with a small maple leaf above the 'a'.



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## Abstract

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The intense maritime military activities, such as live fire training, capabilities assessment or even war, can incur damage to the environment. Numerous ships have sunk through the years in Canada's territorial waters. The ammunition stock that sank with them is likely to liberate contaminants in the aquatic environment. In this context, two separate studies were conducted, with the objective of collecting water and sediments samples in order to detect potential contamination by explosives or heavy metals. The first study was conducted at Point Amour, Labrador, where HMS Raleigh ran aground in 1922. Unexploded ordnances were present and *in situ* detonation was performed. Divers performed sampling before and after each detonation, along with a control site. The second study was conducted in the Halifax Harbour area, where two shipwrecks and one ammunition dumping area were considered. For this study, water and sediments sampling were performed, using a remote operation vehicle (ROV) at various spots in order to find contamination. For the Raleigh operation, trace levels of explosives were detected after detonation events. In the Halifax study, analyses showed no contamination by EM, but some high levels of metals, such as lead, were detected in sediments samples. Those two studies have demonstrated the importance of significant factors, such as sample manipulation and identification, weather conditions and sampling methods in deep water.

## Résumé

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Les nombreuses activités maritimes militaires, telles que l'entraînement au tir réel, l'évaluation des capacités de défense ou encore la guerre, peuvent occasionner de sérieux dommages à l'environnement. Plusieurs navires ont sombré dans les eaux territoriales canadiennes au fil des ans. L'amoncellement de munitions qui a coulé avec ces navires est susceptible de libérer des contaminants dans l'environnement aquatique. Dans ce contexte, deux études différentes ont été menées, avec comme objectif de prélever des échantillons d'eau et des sédiments marins afin de détecter une contamination potentielle par les explosifs ou les métaux. La première étude a été menée à Pointe Amour, au Labrador, où le HMS Raleigh sombra en 1922. Des munitions non éclatées s'y trouvaient et on a procédé à la détonation *in situ* de ces munitions. Des plongeurs se sont chargés de recueillir des échantillons avant et après chaque détonation sur le site, de même que sur un site de contrôle. La deuxième étude a été effectuée à Halifax, où se trouvaient deux épaves de navires de guerre de même qu'un dépotoir de munitions. Au cours de cette opération, l'échantillonnage d'eau et de sédiments a été effectué à l'aide d'un véhicule submersible télécommandé. En ce qui concerne l'opération Raleigh, des traces d'explosifs ont été détectées dans quelques échantillons après la détonation. Pour ce qui est de l'étude menée à Halifax, les analyses n'ont montré aucune contamination par les matériaux énergétiques, mais certains métaux lourds, tels que le plomb, ont été détectés dans les échantillons de sédiments. Ces deux études ont su démontrer l'importance de facteurs significatifs, tels que la manipulation et l'identification des échantillons, les conditions météorologiques ainsi que les méthodes d'échantillonnage en eau profonde.

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## Executive Summary

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Recently, the Canadian government, in conjunction with the Maritime Forces Atlantic (MARLANT), has been concerned by the great amount of shipwrecks and ammunition that are present in its territorial waters.

The first situation happened in the mid-nineties in Point Amour, Labrador, when local residents discovered ammunition shells rolling on the beach. With further inspection, it was discovered that the shells were in fact UXOs, and that the safety of local residents may be endangered by the close presence of these objects. The UXOs were coming from the wreck of HMS Raleigh, a Royal Navy cruiser that ran aground in 1922. The main objective of the HMS Raleigh operation, conducted 6-15 May 2002, was the safe disposal of UXOs present in the area. Another objective of the operation was to assess if the underwater detonation of the UXOs spread explosives residues into the environment. To accomplish this objective, the site was sampled before the demolition work, the UXOs were detonated in place, and then, the site was sampled again in order to verify if contamination by explosives occurred during the operation. Since most of the UXOs were close to the shoreline (50 feet) and that depth was not considerable (30-40 feet), divers were employed to do the underwater work. Sampling was done by the divers directly in the specific containers. The most important observation that came out of this study was that samples were poorly manipulated (labelling and shipping), but traces of HMX, RDX, TNT and ADNT were still found in some samples.

The second operation that was put in place by MARLANT involved more logistics and experimental considerations. This operation was held at sea in the Halifax Harbour area and approaches, November 25th to December 5th, 2002. For this study, three sites were identified. The first one is the wreck of HMCS Clayoquot, a Bangor class minesweeper that was torpedoed by a U-Boat off the coast. The second site is the wreck of SS Kaaparen, a Swedish merchant ship that sunk in collision off the coast during World War II. Finally, the third site is a munitions dumping area, located in Emerald Basin, approximately 50 nautical miles (NM) from Halifax. The purpose of this study was to collect water and sediment samples at each site, along with some bottom observation. Sampling was done with the help of the Deep Seabed Intervention System (DSIS), fitted onboard a Maritime Coastal Defence Vessel (MCDV). Results of the analyses showed that no contamination by explosives was detected in both water and sediment samples. However, all sediment samples presented results for lead (Pb) that exceeded the CCME ISQG. Since the water depth was important (200-600 ft), this operation is considered to be the first known attempt America-wide to sample EM-contaminated sediments in deep ocean. With weather conditions prevailing in November in North Atlantic, it was noted that sampling is more difficult when the ship cannot hold a stable position at the surface. For this reason, it would then be recommended to always perform future similar studies in late spring or summer time, when winds are weaker. This report describes mainly the results from these studies.

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## Sommaire

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Récemment, le gouvernement du Canada, de concert avec les Forces maritimes de l'Atlantique (MARLANT), s'est montré préoccupé par le nombre grandissant d'épaves et de munitions désuètes présentes dans ses eaux territoriales.

La première situation d'importance est apparue en 1994 à Pointe Amour, Labrador, lorsque des habitants ont découvert des obus sur la plage. En inspectant davantage, on a découvert que ces obus étaient en fait des munitions non éclatées (MNE), et que la présence de ces objets pouvait être dangereuse pour la sécurité des habitants. Ces MNE provenaient de l'épave du HMS Raleigh, un croiseur de la marine britannique qui s'est échoué en 1922. L'objectif principal de l'opération Raleigh, effectuée du 6 au 15 mai 2002, était d'éliminer de façon sécuritaire les MNE présentes dans cette région. Un autre objectif de l'opération était d'évaluer si la détonation sous-marine des MNE dispersait des résidus d'explosifs dans l'environnement. Pour atteindre cet objectif, le site a été échantillonné avant les travaux de démolition, les munitions ont été détonées sur place et le site a ensuite été rééchantillonné pour vérifier si une contamination par les explosifs était apparue pendant l'opération. Étant donné que la majorité des munitions se trouvaient près de la rive (moins de 50 pieds), et que la profondeur n'était pas considérable (30-40 pieds), des plongeurs se sont chargés d'effectuer le travail sous-marin. L'échantillonnage a été fait par les plongeurs, directement dans les bouteilles. Les observations les plus pertinentes qui ressortent de cette étude sont que les échantillons ont été mal manipulés (étiquetage et livraison), mais malgré tout, on a découvert des traces de HMX, RDX, TNT et ADNT dans quelques échantillons.

Dans la deuxième opération mise en place par MARLANT, un plus grand nombre de facteurs au point de vue de la logistique et de la méthode expérimentale entraient en ligne de compte. Cette opération a eu lieu dans la région d'Halifax et les environs, du 25 novembre au 5 décembre 2002. Trois sites ont été choisis pour cette étude. Le premier site était l'épave du NCSM Clayoquot, un dragueur de mines de la classe Bangor qui a été torpillé par un U-Boat près des côtes. Le deuxième site était l'épave du SS Kaaparen, un navire marchand suédois qui a coulé à la suite d'une collision près des côtes. Le dernier site retenu était un dépotoir de munitions situé à Emerald Basin, à environ 50 milles nautiques de Halifax. L'objectif de cette étude était de recueillir des échantillons d'eau et de sédiments à chaque site tout en faisant de l'observation sous-marine. On a procédé à l'échantillonnage à l'aide du Deep Seabed Intervention System (DSIS), à bord d'un navire de défense côtière (MCDV). Les résultats des analyses ont démontré qu'aucune contamination par les explosifs n'avait été détectée dans les échantillons. Cependant, tous les sédiments ont montré une teneur en plomb supérieure aux critères CCME pour les sédiments. Étant donné que la profondeur de l'eau était importante, cette étude est considérée comme la première tentative en Amérique d'échantillonnage de sédiments contaminés par les matériaux énergétiques en eau profonde. Compte tenu des conditions météorologiques qui prévalaient en novembre dans l'Atlantique nord, on a noté que l'échantillonnage était plus difficile lorsque le bateau est instable à la surface. Pour cette raison, dans le futur, on recommande de refaire ce genre d'étude à la fin du printemps ou en été, quand les vents sont moins forts. Le présent document décrit principalement les résultats de ces études.

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# 1. Introduction

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The Halifax area is known for its highly important maritime activity. The Port of Halifax is the most important harbour in the Atlantic region of Canada, and the maritime traffic in this region raises around 11% of the total maritime traffic in Canada. Moreover, Halifax hosts the military dockyard, which is the home of several warships that have been transiting in wartime and peacetime operations since the eighteenth century. During the two World Wars, Halifax was a strategic point for the organization of convoys to transit the Atlantic. Due to particular reasons, a considerable number of ships have sunk throughout the years, and some of them were carrying important ammunition stocks. One of the most obvious examples is the Halifax explosion in 1917, when the collision of two military ships, the Belgian *Imo* and the French *Mont Blanc*, resulted in the world's largest accidental explosion. The *Mont Blanc* was a cargo vessel, which was carrying at that moment approximately 35 tons of benzol, 300 rounds of ammunition, 2,300 tons of picric acid and 400,000 tons of trinitrotoluene (TNT). During this tragedy, the entire north end of the city was destroyed, killing over 2,000 people and injuring another 9,000. The Halifax explosion and the other events leading to sunk ships resulted in the spreading of munitions at the bottom of the sea. Another common practice in wartime was to dump ammunition in the ocean when not further needed or in case of enemy's boarding. Sea dumping was practiced by many countries and is now banned. As a result, in many parts of the world, sea dumps are found and can contain very large quantities of unfired items that are found sitting at the bottom of the ocean. In these sea dump areas, where sediments often cover the areas as a result of particle movement and sedimentation in water, the items are slowly corroding. These ammunitions contain explosives such as trinitrotoluene (TNT), picric acid, RDX and HMX, which will eventually leak in the ocean following perforation by corrosion, and increase risks of contaminating sea life involved in the food chain. Furthermore, the shells and the fuzing systems contain metals that are slowly dissolved in sea water. This can represent an important adverse impact to the marine environment.

For these reasons, the interest regarding underwater unexploded ordnance (UXOs) is constantly increasing, and research in this domain is still very recent. Many high-quality works have been accomplished around Emerald Basin, an area that is of great concern in this study. The reports that have been produced were concerning pockmarks [1-3]. Indeed, the presence of those cone-shaped channels is an important characteristic of Emerald Basin, and relation with ammunition lying in this area is not well documented. More recently, one of the major concerns about underwater UXOs was the detection of the source of contamination and further characterization of the plume. Scientists from Nomadics inc. developed a detection apparatus that can help in resolving this difficulty [4]. Their system utilizes amplifying fluorescent polymer (AFP) technology to reflect TNT emissions in aquatic environment. In 1998, a study was conducted in Halifax Harbour, off Rent Point [5]. Sediments samples were collected by divers near live underwater UXOs dating from World War II, and results showed that some of them gave good explosives signatures at the ppb level. A similar study has been conducted in 2001 by scientists from Sandia Corporation [6]. The

objective of this work was to develop a field portable chemical sensing system that could be used to examine underwater UXOs in order to detect any traces of explosives and discriminate between live or inert munitions. However, up to now, the technology has been developed in relation to shallow water, where influences of microbiological and photodegradation activities are more extensively documented than in deep ocean. The present document covers both faces of the situation, that is, UXOs in shallow water and old non-detonated ammunition in deep water.

The first case that held attention was concerning shallow underwater UXOs found at Point Amour (Labrador). HMS Raleigh, a British cruiser, ran aground in this area in 1922. Salvage and scuttling operations did not clear all ordnance from the wreck, and shells were discovered close to the shoreline (50 feet), in water depths varying between 30 and 40 feet. After standard environmental assessment and review of current Canadian regulations concerning aquatic habitats (Fisheries Act), in situ detonation was considered. The test shot operation was held in May 2002 and in May-June 2003. A control site was designated in order to compare the contamination before and after each detonation. Divers were employed to perform water and sediments sampling.

Finally, the purpose of the sampling campaign, which was held in Halifax on November 25 – December 05, 2002, was to take sediments and water samples at strategic spots in shipwrecks and sea dump areas, in order to determine if contamination occurred over the past years. Both metals and explosives were screened to verify the quality of the sediments and water surrounding the sample locations. There were two shipwrecks considered in this study. The first one, HMCS Clayoquot, is located about 15 nautical miles (NM) south from Halifax Harbour. The second one, SS Kaaparen, is located about 10 NM south from Halifax Harbour. Both were believed to carry ammunition at the moment of their sinking. The sea dump area is located in Emerald Basin, which is around 50 NM from Halifax Harbour. The amount of ammunition dumped in this area is still unknown. Samples were collected to evaluate the extent of the contamination, and metals and EM concentrations in both sediments and water were analyzed. At the period of the year when this study was held, the weather was mostly windy with temperatures averaging 5°C during the day and -5°C during the night. However, wind chill factor was considerable everyday, which resulted in a much more difficult sampling campaign.

This study was performed under the work breakdown element 12ny01, “Characterization of DND Sites Contaminated with Energetic Materials,” and was sponsored mainly by DGE and by DRDC Valcartier. All the work performed in both studies was performed in collaboration with the Maritime Forces Atlantic (MARLANT). The work performed at the Halifax Harbour area was also done in collaboration with the Biotechnology Research Institute (BRI) who needed the sediments for microbiology assessment. DRDC Valcartier and BRI have both developed expertise in the characterization and the environmental fate of energetic materials in Canadian Forces training ranges and open detonation ranges.

## **2. Description of Sites**

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### **2.1 Op Raleigh Test Shot Site**

The site designated for Op Raleigh was the wreck of HMS Raleigh, a British cruiser that ran aground at Point Amour, near Forteau, Labrador, in 1922. The wreck is located within 30 feet from the shore, in approximately 40 feet of water. UXOs are present around the wreck, and TNT is the main explosive concerned. A detonation site was designated at approximately 60 feet west from the wreck and a control site was designated at approximately 100 feet northwest from the detonation site. Bottom type is mostly silt and rocks. Figure 1 in Annex 1 shows the working area along with the position of the wreck.

### **2.2 Halifax Sampling Sites**

Three sites were considered in the Halifax campaign. The first two sites are shipwrecks, HMCS Clayoquot and SS Kaaparen, and the third site is a munition dump located in Emerald Basin. Figure 2 (Annex 1) shows the position of these three sites.

#### **2.2.1 Wreck of HMCS Clayoquot**

HMCS Clayoquot was a Canadian Bangor class minesweeper that was torpedoed by a U-Boat in 1944. The ship was carrying two 20-mm guns along with a 12-pounder gun. The wreck is located approximately 3 nautical miles (NM) south from Halifax, in 270 feet of water. UXOs are believed to be present containing mainly TNT as the explosive charge. Bottom type in this area is thick silt and clay.

#### **2.2.2 Wreck of SS Kaaparen**

SS Kaaparen was a formerly Norwegian warship that was sold to the Swedish navy. The ship sank in 1942 after a collision during a convoy organization. No specific data was available concerning the type of ammunition carried onboard this ship. The wreck is located approximately 1 NM north from the wreck of Clayoquot, on rocky bottom.

#### **2.2.3 Emerald Basin Dumping Area**

Several magnetic anomalies have been recorded in Emerald Basin, possibly due to the presence of underwater UXOs. During past military activities, numerous cases of munitions dumping have occurred in this area. The total amount of ammunition lying underwater is still unknown. Emerald Basin is a very deep area, averaging 600 feet of water. Bottom type is a blend of

stratified Emerald silt and loosely compacted LaHave clay. Emerald Basin covers a very large area, but for the sake of this study, a 2.5 km<sup>2</sup> circular area of operation presenting strong magnetic anomalies was designated.



### 3. Strategies and Methods

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#### 3.1 Op Raleigh

The underwater UXOs found around the wreck of HMS Raleigh were 7.5-inch projectiles containing mainly Lydite, TNT or black powder (see Figure 3, Annex 1), 3-inch projectiles, small arms munitions, Cordite etc. In order to safely dispose of these UXOs, high order detonation had to be achieved. This was evaluated through a test shot operation in May 2002 by using three 2-lb blocks of C4 on each projectile. The operation implied the destruction of fifteen projectiles, with pre- and post-detonation sampling. A control site was also designated for sampling, as a base of comparison for the contaminants dispersion.

Water and sediments sampling was performed by divers. The sample collection was done directly in the sampling container. Water samples for energetic materials analysis were collected directly in amber glass bottle (1l), water samples for metals analysis were collected in polyethylene bottles (250 ml), and sediment samples were collected in glass and Teflon liner jars. The pre-detonation samples were collected as follows: five sets of samples around the detonation site (one set of samples corresponding to one sediment sample, one energetic materials water sample and one metal water sample), collecting a sample at the center of a 10-m radius circle plus four samples according to cardinal points around the circle; five sets of random samples around the wreck site where the ordnances were sitting; and one set of samples at the control site as a base of comparison. Post-detonation samples were collected at the detonation site, according to the same circular pattern, and at the control site. The post-detonation samples were collected 30-45 minutes after the detonation due to safety considerations but may represent a drawback of this study since the contaminants had plenty of time to disperse and underestimate the concentrations resulting from the detonations. Immediately after each sampling, energetic materials water samples were stabilized with 1.5 g of sodium bisulfate, whereas metals water samples were treated with 15-20 drops of a solution of 20% nitric acid. Containers were stored in a refrigerator at 4°C and later stored in a plastic cooler filled with ice packs for shipment to the laboratory for metal analyses and to DRDC Valcartier for explosives analyses.

In May-June 2003, a second test shot operation was conducted and samples were collected for explosive analyses. The same sample treatment was done as before during the first test shot operation. Since the HMS Raleigh wreck covers a reasonably large area of the ocean floor, it was necessary to break up the site into various zones. All detonations were conducted in Zone 1. No picture or figure illustrating this zone is available. The Zone 1 consisted in 9 squares of 3 x 3 m disposed on three rows where from left to right on the first row, squares A, B and C were found, D, E and F on the second row and G, H and I on the third row. Samples were collected in each of those squares before detonation (21 May 2003), after detonation (26 May 2003) and one week later (2 June 2003) meaning 27 samples. On top of these 27 samples, three background samples were collected from areas that are believed to be unaffected 500

m away from Zone 1. Due to weather conditions, background locations were not re-sampled after detonations. In total, 30 sediments samples and 30 water samples were received at DRDC Valcartier for explosive analyses.

A	B	C
D	E	F
G	H	I

To locate the position of all the squares within Zone 1, the GPS locations were noted and are as follows:

Square A: N 51 27.536 W 56 52. 233 depth 6.4 m

Square B: N 51 27.522 W 56 52. 234 depth 4.7 m

Square C: N 51 27.509 W 56 52. 232 depth 4.0 m

Square D: N 51 27.540 W 56 52. 247 depth 6.1 m

Square E: N 51 27.536 W 56 52. 245 depth 4.9 m

Square F: N 51 27.514 W 56 52. 250 depth 3.7 m

Square G: N 51 27.541 W 56 52. 260 depth 6.1 m

Square H: N 51 27.535 W 56 52. 262 depth 6.4 m

Square I: N 51 27.524 W 56 52. 264 depth 3.0 m

The background samples were named according to the sample direction away from Zone 1 meaning that a north, a south and a west sample were collected. Since they were only 25 m off shore, it was not possible to collect an east background sample. The GPS locations of the background samples were also noted and were respectively N 51 27.438 W 56 52.829 at a depth of 1.8 m for the south sample and N 51 27.746 W 56 52.513 at a depth of 0.4 m for the west sample. No GPS data is available for the north background sample.

### 3.2 Halifax Operation

The sampling was done with the use of a Deep Seabed Intervention System (DSIS) carried onboard a Maritime Coastal Defence Vessel (MCDV) of the Canadian Navy. The DSIS is comprised of a Remotely Operated Vehicle (ROV) fitted inside an

aluminium cage. This cage was brought in the water by a motor-operated winch containing 1,000 m of cable. The ROV was deployed from the cage at short distance from the bottom of the sea and was connected via 250 m of tether. The submersible part of the system was controlled and monitored from a Control Van (CV). The ROV is fitted with 2 arms; one capable of 7 functions and the other, of 5 functions. Those arms were controlled from the CV. Follow-up was done by watching one of the camera displays in the CV. Figures 4, 5 and 6 in Annex 1 show the system and its layout.

Water sampling was done by using 6-ganged PVC bottles each containing 1.2 l. These bottles contain a cap at each end: they are joined together with an elastic rubber tube inside the bottle (see Figure 7, Annex 1). Before sending the sampler in the water, the two caps had to be manually opened and attached to the piston activator located at the middle of the bottle. The flush valve found at the bottom of each bottle also had to be closed and the pressure seal tightened. Once the sampling system was ready, the bottles were cleaned using acetone then rinsed with distilled water. Once cleaned, the sampling system was brought to the ROV, where one of the two arms could take it in its claw. The other arm of the ROV was fitted with an aluminum stick, which was used to activate the pistons of the bottles in order to capture the water inside. Sampling method originally consisted of taking a water sample at 4 cardinal points on a 50-m radius circle around the target, with at least 25% of random duplicates. Once the samples had been taken, the sampler was brought back onboard and the samples were split into portions for energetic materials (EM) and for metals analyses. The EM water samples were transferred into a 1 l amber glass bottle containing 1.5 g of sodium bisulphate. The metals water samples were transferred into a 250 ml plastic bottle containing 1 to 2 ml of a solution of 50% nitric acid. These bottles were stored in a cooler on the sweep deck during sailing, and then transferred in a refrigerator when back on land.

For the sediment sampling, two methods were used, depending on the type of sample needed. The first method was core sampling, using aluminum tubes containing about 500 g. These core samplers were used to take samples at cardinal points around the target, in the same way as for the water samples. The core samplers were disposed in a rack containing PVC tubes with a rubber stopper at the bottom. Before fixing the sampler on the ROV, aluminum tubes were cleaned with acetone and nitric acid, and rinsed with distilled water between each cleaning step. The PVC tubes and rubber stoppers were cleaned with acetone and rinsed with distilled water. Once the sampler was back onboard, the samples were split into portions for energetic materials (EM) and for metals analyses transferred in plastic bags using a small metallic scoop, which had been previously cleaned according to the precedent description. The plastic bags were then stored in a cooler on the sweep deck, until back on land where they were transferred in a freezer. Since a large sediment sample was needed by BRI for microbiology study, a second method was developed to collect such a large sample. This second method used for sediment sampling consisted of scooping the bottom of the ocean with a large aluminum container, in order to fill a 20 l plastic pail. Interestingly, this unsophisticated method worked well and the plastic pail was easily filled with sediments. The container was also previously cleaned with acetone then nitric acid, and rinsed with distilled water between steps. Figures 8 and 9 (Annex 1)

show the sediments samplers for both methods. Once back onboard, the sample was simply transferred by pouring the content in the pail. The pail was then stored on the sweep deck for all the length of the study. Due to cold weather, the sediment sample in the pail slowly froze over the length of the trip. All samples were then shipped to Biotechnology Research Institute (BRI) in Montreal for analysis of EM and microcosm studies and, to a private laboratory in Halifax for metals analyses.

### 3.3 Analytical Chemistry

Most of the analyses of EM samples were performed at DRDC Valcartier except for the Halifax Operation samples that were done at the Biotechnology Research Institute (BRI). Both Laboratories used the High Pressure Liquid Chromatography (HPLC), according to the US EPA Methods 8330A (sediments) and 3535A (pore water and sampled water) see the Environmental Protection Agency internet site ([www.epa.gov](http://www.epa.gov)) for a complete description of these methods. For metals, the analyses was done by Inductively Coupled Plasma/ Atomic Emission Spectroscopy (ICP-AES), according to the ASTM Method D3974, Preparation III, Digestion A and were performed by private laboratories.

For the Op Raleigh samples for energetic materials analyses were treated and analyzed as follows by DRDC Valcartier: For the analysis of sediment samples, they were treated as soils, they were then dried in the dark, homogenized by adding acetone to form a slurry which was then evaporated. Soils were sieved through 25 mesh sieves. From the sieved sediments, eight grams were mixed with acetonitrile (10 mL) and a vortex was applied for one minute, followed by a sonication period of 18 hours after which the samples were left to settle for 45-60 minutes. The mixture was then filtered on a 0.45 microns filter and a precise 2 ml of the extract was sent to the Zymark apparatus for complete evaporation. Once dried, the residue was dissolved with acetonitrile (0.5 ml) that was placed in a vial to be mixed with distilled water (0.5 ml). These extracts were then analysed using the HPLC 8330 method. For each sample, a replicate was done and analysed. For all the water samples, paper filtration was done to remove excess salt and small rocks. The filtered samples were then passed through a sep-pack for adsorption. When available, 500 ml of water was passed through the sep-pack but for most of the water samples, limited volumes (100-250 ml) were available and all the quantity was passed through the cartridge and this quantity was taken into account into the calculations. The adsorbed explosives were extracted by passing acetonitrile (5 ml) through the sep-pack and from this 1 ml was introduced in a vial and diluted with 1 ml of distilled water. These extracts were then analysed using the HPLC 8330 method. For each sample, a replicate was done and analysed.

For the Halifax operation, samples for energetic materials analyses were treated and analyzed as follows by BRI: For the analysis of sediment samples, the water content (wt. %) was determined in the 3 samples at the sea dump and found to be  $55.0 \pm 0.3\%$  for S-SD-20L,  $54.6 \pm 0.9\%$  for S-SD-1 and  $53.2 \pm 0.6\%$  for S-SD-2. The sediments samples were centrifuged to collect pore water and the pH of the pore water was measured at 7.75 for S-SD-20L, at 7.64 for S-SD-1 and at 7.62 for S-SD-2. The solid residues resulting from centrifugation were dried under the fume hood and were

extracted with acetonitrile ( $\text{CH}_3\text{CN}$ ) according to US EPA Method 8330A using 40 ml of  $\text{CH}_3\text{CN}$  for 16 g of sediment instead of 10 ml for 2 g of soil as recommended in the method. Extracts were analyzed by HPLC for TNT, RDX, and HMX. No traces of explosives or degradation products (amino- and nitroso-compounds) were found in these samples by BRI (Limit of Detection (LOD) (TNT) < 0.1 ppm; LOD (HMX) < 0.25 ppm). The volume of pore water collected from each sample (34 ml) was extracted by Solid Phase Extraction according to US EPA method 3535A to yield a 5 ml  $\text{CH}_3\text{CN}$  extract. Extracts were analyzed by HPLC for TNT, RDX, and HMX. No traces of explosives or degradation products (amino- and nitroso-compounds) were found (LOD < 15 ppb). For each water sample a quantity of 500 ml was extracted by Solid Phase Extraction according to US EPA method 3535A to yield a 5 ml  $\text{CH}_3\text{CN}$  extract. Extracts were analyzed by HPLC for TNT, RDX, and HMX. No traces of explosives or degradation products (amino- and nitroso-compounds) were found (in these cases, LOD < 1 ppb).

## 4. Samples Analyses and Results

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For both operation Raleigh (May 02) and Halifax operation, total metals and energetic materials were analyzed in both water and sediments samples. Unfortunately, no metal analyses were performed on the sediments and water samples collected during the second test shot operation performed in Labrador in May 2003.

### 4.1 Op Raleigh

Five sets of samples were collected for this trial in May 2002

1-	Ship site (before detonation)	BS
2-	Detonation site (before detonation)	BD
3-	Detonation site (after detonation)	AD
4-	Control site (before detonation)	BC
5-	Control site (after detonation)	AC

In general, trace quantities of either TNT or HMX were found in the sediments or in water samples. Assuming that the ordnances were old and contained only TNT, picric acid or tetryl, HMX presence might be explained by the use of C4 (91 % RDX and 9 % of wax), which contains HMX as an impurity of RDX (up to 15 % of HMX into RDX). HMX has a very low solubility in cold saline water (less than 4 ppm) and might therefore be more persistent in the environment since it is not dissolved and diluted.

For the second test shot operation in May 2003, as explained earlier, three sets of 9 samples were collected in 9 squares A to I composing Zone 1. On top of these samples, 3 background samples were collected before detonation in the north, west and south direction 500 m away from Zone 1. All the explosive analyses for these 30 samples revealed no explosives. Since no metal analyses were performed on these samples, no results are available.

#### 4.1.1 Water

Results for explosives concentrations into water samples are presented in Table 1 (Annex 2). Water samples were poorly labelled and four of them had to be guessed since their labels were almost erased during shipment. Two samples (BS3 and BS5) were not analyzed due to an insufficient volume for extraction and further analyses.

- No HMX was detected in the water samples which is not surprising due to its low solubility;
- AC sample showed traces of TNT, RDX and amino DNT's and this was somehow surprising since it implies that explosives moved from the detonation area to the control site which was remote from the site. The same area sampled before detonation (BC) showed no traces of explosives.
- TNT was detected in 5 samples including AC, but at trace levels only. No explosives were found in BD and this was normal and foreseen while the TNT concentrations were measured in AD samples, which demonstrated that traces of TNT were potentially released during the shots. TNT was also found at the ship site before detonation and this can indicate that some UXOs are presently leaking explosives. In all cases, the explosives were found at trace levels and this is normal since the dilution factor in the ocean is very important.

For metals in water samples, nothing conclusive could be obtained from the analyses, since all the levels did not change before or after the detonation, the detonation did not seem to affect the metal concentrations in water. One should keep in mind that the detonations break into smaller pieces the original ordnances and therefore increase the metallic surface exposed to water which may lead to a faster dissolution of metals and eventually to greater metals concentrations in water.

#### **4.1.2 Sediments**

Results for explosives concentrations obtained for sediment samples are presented in Table 2 (Annex 2). Six samples were not analyzed due to the breaking of the jars during the shipment. HMX was detected in 3 samples:

AC: traces of HMX present after detonation at the control site (surprising).

AD3: Traces of HMX after detonation at the disposal site.

BS1: Traces of HMX (surprising).

No TNT was observed using a quantification limit of 100 ppb, HMX was found at the control site and also at the ship site, which was unexpected if we consider that no munitions contained HMX. Since the explosive analyte was detected at trace levels, we have no valid explanation for those results, so cross-contamination or laboratory contamination might be a significant factor in these instances.

## 4.2 Halifax Operation

Due to specific weather conditions at this time of the year, sampling did not occur exactly as described in the previous section. The next paragraphs include more details about the specific operations accomplished during this study. First, it is important to mention that due to the bad weather conditions and time constraint, one of the shipwrecks, the SS Kaaparen, was not visited at all, thus no samples have been collected for this site.

### 4.2.1 Sampling at the HMCS Clayoquot Wreck

The only shipwreck visited was the HMCS Clayoquot, which was found at a depth of approximately 270 ft. Because of time and weather conditions, only water sampling was performed at this site. Moreover, the four cardinal points technique could not be applied thoroughly, since maintaining the ship stable at the surface was difficult due to strong winds. However, four water samples were taken at this site, split for EM and metals analyses, and distributed as follows :

- Sample 1 (identified W-SW1-1): Off the Port bow, forward part of the ship, sample was taken approximately 3 m from the wreck and 1 m from the bottom.
- Sample 2 (identified W-SW1-2): Off Port midships, in line with the bridge, sample was taken approximately 3 m from the wreck and 1 m from the bottom.
- Sample 3 (identified W-SW1-3): Off the Port stern, close to what was believed to be a depth charge, sample was taken approximately 50 cm from the barrel and 30 cm from the bottom.
- Sample 4 (identified W-SW1-4): Off the Starboard stern, on the deck, close to what looked like an empty 20-mm casing, sample was taken approximately 30 cm from the casing and from the bottom. Sample 4 was duplicated both for EM and metals, for 25% of reproducibility in the samples.

Figure 10 (Annex 1) shows the sampling pattern around the wreck. Analysis of those samples showed no contamination by either EM or metals. Table 3 (Annex 2) presents the results of metals analyses.

### 4.2.2 Sampling at the Dumping Area in Emerald Basin

The dumpsite located in Emerald Basin is a very large and deep environment (depth is approximately 600 ft), characterized by a thick silt and mud bottom. Again, due to weather, a limited number of samples were taken, but this time both sediments and water were collected. For the sediments, two core samples



were taken along with the 20 l pail, whereas four water samples were collected. As far as possible, the water and sediments samples were collected according to the cardinal points technique, inside a margin of 50-100 m from the center of the circle. It has to be noted that no empty casings or UXO shells were seen during the bottom observation. Also, tracking problems occurred with the beacon installed on the ROV, so the computed position for this site might not be as accurate as believed.

The four water samples were collected, split into EM and metals, and distributed as follows :

- Sample 1 (W-SD-1): East sample, taken approximately 100 m from the target and 3 m from the bottom. Exact location was deviated about 20° clockwise from real East.
- Sample 2 (W-SD-2): West sample, taken approximately 60 m from the target and 3 m from the bottom. Sample 2 was duplicated for the metals sample. Exact location was deviated about 5° counterclockwise from real West.
- Sample 3 (W-SD-3): South sample, taken approximately 120 m from the target and 10 m from the bottom. Sample 3 was duplicated for the EM sample. Exact location was deviated about 10° clockwise from real South.
- Sample 4 (W-SD-4): North sample, taken approximately 75 m from the target and 5 m from the bottom.

Figure 11 in Annex 1 shows the water sampling pattern in Emerald Basin.

For sediments sampling, the situation was more difficult due to poor visibility, since the bottom was so light and sediments were easily dispersed by the presence of the ROV propulsion system. However, two core samples were taken, split into EM and metals, and distributed as follows :

- Sample 1 (S-SD-1): West sample, taken approximately 25 m from the target and at a depth of 30 cm in the bottom.
- Sample 2 (S-SD-2): South sample, taken approximately 35 m from the target and at a depth of 60 cm in the bottom.

Along with those core samples, one 20l plastic pail was filled, after scooping the bottom with a metallic container. This sample was taken approximately 40 m from the target, southwest (see Figure 12, annex 1). Off this large sample, one small duplicate was transferred in plastic bags both for EM and metals (identified S-SD-20L).

Analysis of those samples showed no contamination by either EM or metals for water samples. However, some metal analytes, such as Al, Fe and Pb, were detected at quite high levels in sediments samples. Al and Fe can naturally occur at very high concentrations. However, it would be surprising that lead would occur naturally at these concentrations. It would have been beneficial to collect background samples and compare with the mean levels for each parameters in this geological formation. Since it was not possible to collect background samples at that time, we can not draw any conclusion about the high concentrations of Al, Fe and Pb in these sediments. Table 4 (Annex 2) shows the results of metals analyses in sediments.

#### **4.2.3 Sampling at Parfait Bank in Bedford Basin**

Since time was short and weather conditions were not ideal to go further out to sea, the ship sailed one day in Bedford Basin for a demonstration. The area is called Parfait Bank. At this moment, one water sample was taken at a depth of approximately 30 m (sample was identified W-BB-1). A duplicate sample was made for metals. Analyses of those samples showed no contamination by either EM or metals.

## 5. Discussion

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This section includes several miscellaneous observations that were made during the study and that could be pertinent for the interpretation of results or future similar sampling operations. Also, recommendations are made in order to improve next studies in this domain.

### 5.1 Op Raleigh

Identification of the samples of the first test shot operation conducted in May 2002 was difficult and the results related to these samples were surprising. There were a lot of uncertainties, especially with the water samples, since most of the writing was washed away, and guesses had to be taken to attribute the sample to its label. Moreover, 5 jars of sediments were broken in transport and the cooler was filled with a mixture of unbroken jars, sediments and water. This is a situation where cross contamination between samples may occur, especially when low levels are present.

The results obtained for this campaign should be looked at with great caution since there are only a limited amount of samples. Potential cross-contamination can have occurred and labelling problems were encountered. High concentrations of explosives were not anticipated and were not observed. This can mean that open detonation of underwater UXOs can represent a viable technology to dispose of underwater UXOs but much more samples will have to be taken and more tests will have to be executed before such conclusion can be validated.

Lessons can be learned out of this first trial. The sampling campaign should involve a better sample identification, treatment, segregation and labelling system. Secondly, a shipment system using better precautions should be put in place to avoid breaking the samples. For this study, DRDC representatives were not able to attend to the sample collection and it was difficult to interpret the results not having been on site. An important part of the sample collection is actually to attend the sampling, interpret on the spot the data observed; this is the quantity, the quality of the samples, the number of background, etc. All this orients the collection of the samples to get in the end the best interpretation of valid results that will lead to better conclusions. This situation should be corrected for future sampling if a better understanding of the technology is sought after.

For the second test shot operation, insufficient amounts of sediments or water were received at DRDC Valcartier. Sometimes the samples were of bad quality, too many rocks, not enough sediment or simply not enough material to analyse, making these analyses again very difficult to interpret. When insufficient amounts of material are analysed for explosive detection at trace levels, we are pushing the limits of analytical chemistry and strange results can occur such as explosive detection detected before but not after detonation or worse, not detected after detonation but detected a week later. Combined with the presence of impurities, with the difficulties of performing analyses

at these concentrations and under these conditions, no conclusion can firmly be drawn from these results. During the first test shot, we observed that a safety period was necessary to wait before collecting samples and we mentioned that this time period was favouring the explosives dispersion and dissolution into the ocean. In that sense, collecting samples a week after detonation was useless considering the dissolution factor.

## 5.2 Halifax Operation

Weather, particularly winds, was often not ideal for stabilizing the ship. Thus, the ROV could not be launched since high tensions could be put on the winch cable. Also, cold temperature caused some problems to the telemetry system since one circuit card simply froze overnight. For those two reasons, it is recommended that further sampling operations be conducted in the summer time, when winds will be less important and weather will not be a considerable factor for the system. However, doing such a campaign in the summer would imply finding an appropriate area in the ship to store the samples, since samples have to be kept at 4°C.

The manipulation of the arms from the CV requires high hand-eye coordination and great reflexes. During the operations, the sampler often bumped into objects or the bottom, and samplers were then broken or lost at the bottom. This type of incident could lead to cross-contamination between samples or loss of important samples. In order to minimize the risk of mistakes, it is recommended to affect two highly trained personnel (one for each arm) that could manipulate the arm in different conditions and thus bringing more accuracy to the sampling. Moreover, when DSIS had some operational difficulties, it was often impossible to fix the problem right away and carry on with the rest of the study, due to a lack of spare parts onboard. It is recommended to verify thoroughly the spare parts list for the system and make sure that these parts are available on board when needed.

Water sampling using the ganged bottles sampler worked fairly well. However, it happened sometimes that samples were lost due to bad sealing of the caps after closure. To prevent that, the length of the elastic rubber tube joining the two caps must be accurately measured. Also, the pressure seal at the top of each bottle must be fitted with an O-ring and well tightened before each dive. Another concern about the use of PVC bottles for sampling is the interaction with organic compounds. Literature has proven that PVC should not be used for water sampling, since organics can diffuse in its microstructure [7]. Teflon sampling and storing bottles should be employed.

Sediment sampling with core samplers seemed difficult, mainly because the alignment of the sampler in its tube was difficult. Also, core samplers were not put back inside their original tube, thus opening the way to cross-contamination or error in sample identification. Manipulating the arm with more flexibility and concentrating on putting the core samplers back in the same tube as where it was taken would preserve accuracy in sample collection and identification. As for microbiological analysis, collecting core samples in this way is not preferable, since the sample has to be transferred into another container after its collection and oxygen will affect the integrity of the sample.

Perfectly sealed grab samples or core samples kept in the collection position would be more advisable. The collection of a large volume of sediments by scooping the bottom with a metallic container worked surprisingly well for the sea dump area, because the bottom was soft. However, the container was virtually not fitted with a lid that could appropriately seal the sample when bringing it back at the surface. At the end of the study, another similar equipment was brought onboard, this time fitted with a lid, but time was insufficient to verify the performance of this equipment. For future studies, scooping the soft bottom with a large container could still be performed, but the lid should be perfectly sealed in order to prevent circulation of water through the sediment when bringing it back at the surface. Also, a grab sampler that could fit in one of the claws of the ROV would be an ideal piece of equipment, since it perfectly seals the sample.

Since no EM contamination was detected in water or sediments samples, experimental methods should be reviewed. In this context, efforts should be put on bottom observation and localization of ammunition, especially in Emerald Basin. Sedimentary rate should be accurately measured and depth of the ammunition in the sediments should be determined, in order to sample close to the ammunition. With regards to shipwrecks, the same considerations apply. Sediments samples should be the priority, since they proved to contain considerable levels of metals. In places where water depth is practicable for divers, one should consider the advantage of accurate sampling by human intervention instead of DSIS.

## 6. Conclusion

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Collection of water and sediments samples close to underwater UXOs has proven to be an extremely difficult task. Compared to other studies conducted in this domain, true attempts were now made in order to dispose of underwater UXOs or to evaluate the contamination at great depths. Disposal operations conducted around the wreck of HMS Raleigh in Labrador showed that trace levels of explosives could be found at the detonation site after the detonation. However, the results are possibly the result of the poor sample handling and identification. The first attempt to collect potentially contaminated sediments in deep sea was done in Halifax, around shipwreck and at a munitions dumping area. Analyses showed that no contamination by energetic materials was detected. However, high concentrations of metals, such as lead, were found in each sediment sample coming from Emerald Basin.

The sampling operations in Halifax, that were mainly conducted on November 26 and 27, allowed the crew to visit one shipwreck and one sea dump to take water and sediments samples, and to familiarize with the equipment and its functional limits. The total number of samples expected was not collected, but this was mainly due to the weather conditions. Observations showed that collecting sediments at a depth of 300 ft and more is a difficult task. The use of the DSIS is appropriate for this type of study, but manipulation skills and repair facilities must be upgraded. The information gained in the present study is relatively scarce and non reliable due to the various factors already enumerated. There is still a strong need to reconsider a similar study based on the knowledge obtained from these studies since we were not able to confirm that underwater detonation does not lead to explosives spreading. Furthermore, assessing the environmental fate of underwater UXOs is very difficult and it is far from being determined. DRDC Valcartier is convinced that more sampling is needed to understand the environmental impacts of underwater detonation and to assess the impacts of the presence of large amounts of items gathered in sea dump areas. More background samples are needed to evaluate the impacts of the corroding shells at sea. Finally, DRDC Valcartier considers that its presence on site is essential to the sample collection and to the gathering of the results.

## 7. References

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## List of Acronyms

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ADNT	Aminodinitrotoluene
AFP	Amplifying Fluorescent Polymer
BRI	Biotechnology Research Institute
CCME	Canadian Council of Ministers of Environment
CV	Control Van
DRDC	Defence Research and Development Canada
DSIS	Deep Seabed Intervention System
EM	Energetic Materials
EPA	Environmental Protection Agency
HMCS	Her Majesty's Canadian Ship
HMS	Her Majesty's Ship
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High-Pressure Liquid Chromatography
ICP-AES	Inductively-Coupled Plasma – Atomic Emission Spectroscopy
ISQG	Interim Sediments Quality Guideline
LOD	Limit of detection
MARLANT	Maritime Forces Atlantic
MCDV	Maritime Coastal Defence Vessel
NCSM	Navire canadien de Sa Majesté
NM	Nautical Miles
PVC	Polyvinylchloride
RDDC	Recherche et développement pour la défense Canada
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
ROV	Remote Operation Vehicle
TNT	Trinitrotoluene
UXO	Unexploded Ordnance



## Annex 1 - Figures

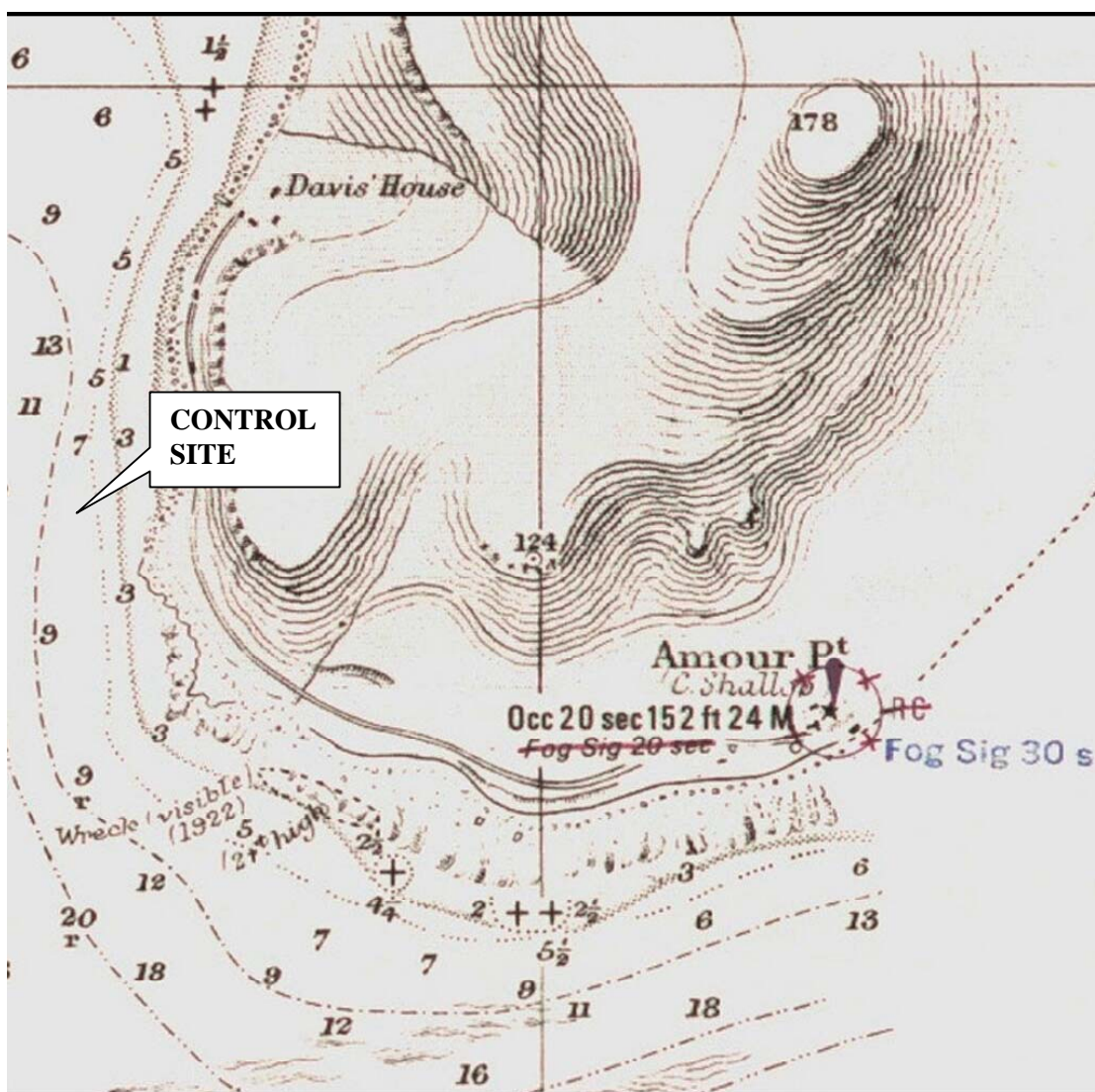


Figure 1. Map of Point Amour Working Area

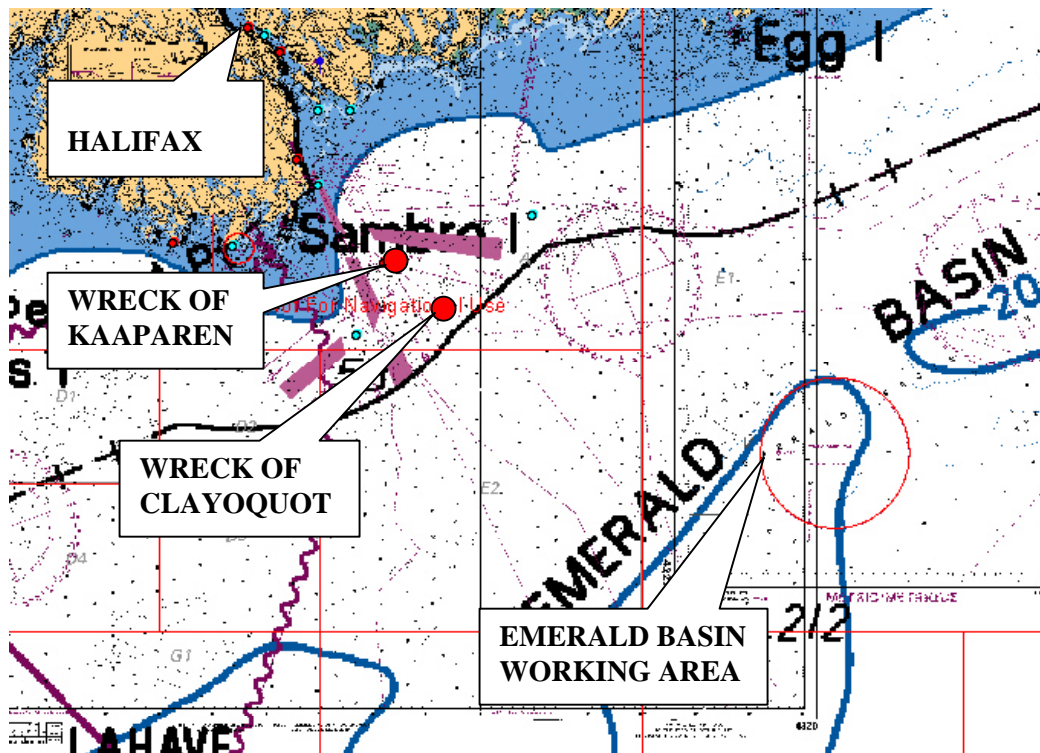


Figure 2. Map of Halifax Working Area



Figure 3. Projectiles Found Around the Wreck of HMS Raleigh



**Figure 4. Layout of DSIS on the Deck**



**Figure 5. Deployment of the ROV**





**Figure 6. Control Van**



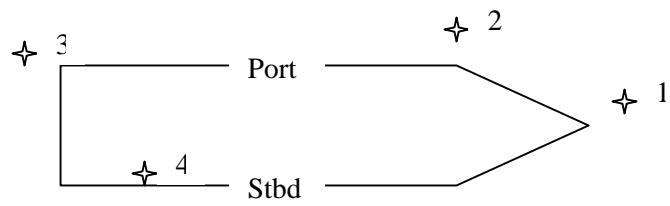
**Figure 7. Water Sampler**



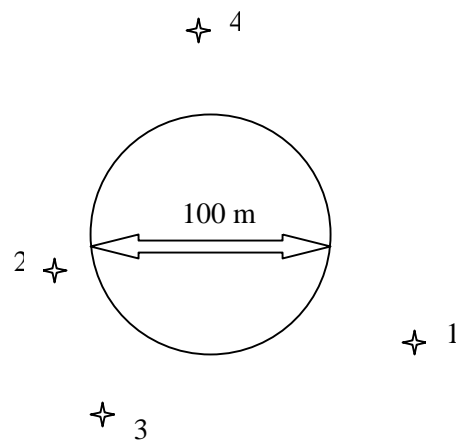
**Figure 8. Core Samplers**



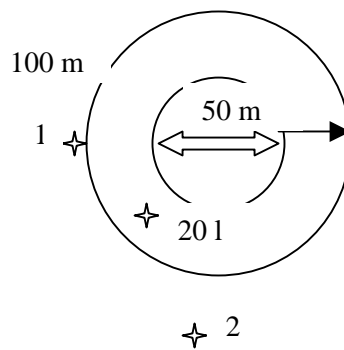
**Figure 9. Metallic Container Used for Scooping Sediments**



**Figure 10. Water Sampling Pattern Around the HMCS Clayoquot Wreck**



**Figure 11. Water Sampling Pattern Around Emerald Basin Dumpsite**



**Figure 12. Sediments (Core and Scooping) Sampling Pattern Around Emerald Basin Dumpsite**

## Annex 2 – Tables

TABLE 1: EM ANALYSES FOR RALEIGH WATER SAMPLES

<b>SAMPLE</b>	<b>2,6-DNT (ppb)</b>	<b>2,4-DNT (ppb)</b>	<b>TNT (ppb)</b>	<b>RDX (ppb)</b>	<b>amino's (ppb)</b>	<b>tetryl (ppb)</b>	<b>HMX (ppb)</b>
BC	n.d	n.d	n.d	n.d	n.d	n.d	n.d
AC*	n.d	n.d	0.001	0.001	0.001	n.d	n.d
BD1	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BD2	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BD3	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BD4	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BD5*	n.d	n.d	n.d	n.d	n.d	n.d	n.d
AD1	n.d	n.d	n.d	n.d	n.d	n.d	n.d
AD2	n.d	n.d	0.001	n.d	n.d	n.d	n.d
AD3	n.d	n.d	n.d	n.d	n.d	n.d	n.d
AD4	n.d	n.d	n.d	n.d	n.d	n.d	n.d
AD5	n.d	n.d	0.002	n.d	n.d	n.d	n.d
BS1*	n.d	n.d	0.001	n.d	n.d	n.d	n.d
BS2*	n.d	n.d	0.002	n.d	n.d	n.d	n.d
BS4	n.d	n.d	n.d	n.d	n.d	n.d	n.d

Detection Limit : 1 ppt

\* : Name was deduced due to erasing of label

n.d. : Not Detected

**TABLE 2: EM ANALYSES FOR RALEIGH SEDIMENTS SAMPLES**

<b>Sample</b>	<b>HMX (ppb)</b>	<b>Tetryl (ppb)</b>	<b>2-ADNT (ppb)</b>	<b>4-ADNT (ppb)</b>	<b>RDX (ppb)</b>	<b>TNT (ppb)</b>	<b>2,4-DNT (ppb)</b>	<b>2,6-DNT (ppb)</b>	<b>1,3-DNB (ppb)</b>	<b>NT (ppb)</b>	<b>NB (ppb)</b>	<b>1,3,5-TNB (ppb)</b>
<b>BC</b>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>AC</b>	117	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BD1*</b>												
<b>BD2*</b>												
<b>BD3</b>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BD4</b>	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BD5</b>	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>AD1*</b>												
<b>AD3</b>	144	n.d.	n.d.	n.d.	n.d.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>AD4</b>	n.q.	n.d.	n.d.	n.d.	n.d.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>AD5</b>	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BS1</b>	142	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BS2*</b>												
<b>BS3</b>	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BS4</b>	n.q.	n.d.	n.d.	n.d.	n.d.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<b>BS5*</b>												

Detection Limit : 5 ppb ; Quantification Limit : 100 ppb

\* : Broken jar, not analyzed

n.d. : Not detected ; n.q. : Not quantified



**TABLE 3: METALS ANALYSES FOR HALIFAX WATER SAMPLES (PPM)**

<i>sample</i>	<i>Ag</i>	<i>Al</i>	<i>As</i>	<i>B</i>	<i>Ba</i>	<i>Be</i>	<i>Bi</i>	<i>Cd</i>	<i>Co</i>	<i>Cr</i>	<i>Cu</i>	<i>Fe</i>	<i>Hg</i>	<i>Mn</i>	<i>Mo</i>	<i>Ni</i>	<i>P</i>	<i>Pb</i>	<i>Sb</i>	<i>Si</i>	<i>Sn</i>	<i>Sr</i>	<i>Tl</i>	<i>U</i>	<i>V</i>	<i>Zn</i>
w-sd-1	n.d.	n.d.	n.d.	4.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.11	0.33	n.d.	6.6	n.d.	n.d.	n.d.	n.d.
w-sd-2	n.d.	n.d.	n.d.	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	0.36	n.d.	6.1	n.d.	n.d.	n.d.	n.d.
w-sd-3	n.d.	0.03	n.d.	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35	n.d.	6.1	n.d.	n.d.	n.d.	0.02
w-sd-3-dup	n.d.	0.02	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.12	0.32	n.d.	6.2	n.d.	n.d.	n.d.	n.d.
w-sd-4	n.d.	0.02	n.d.	4.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	0.06	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	0.10	0.38	n.d.	6.7	n.d.	n.d.	n.d.	n.d.
w-sw1-1	n.d.	0.02	n.d.	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.08	0.29	n.d.	5.8	n.d.	0.2	n.d.	0.07
w-sw1-2	n.d.	n.d.	n.d.	3.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.30	n.d.	5.8	n.d.	0.2	n.d.	n.d.
w-sw1-3	n.d.	n.d.	n.d.	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.30	n.d.	5.7	n.d.	n.d.	n.d.	n.d.
w-sw1-4	n.d.	n.d.	n.d.	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.18	0.31	n.d.	6.5	n.d.	n.d.	n.d.	n.d.
w-sw1-4-dup	n.d.	n.d.	n.d.	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	n.d.	0.30	n.d.	5.9	n.d.	n.d.	n.d.	n.d.
w-bb-1	0.02	n.d.	n.d.	4.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	n.d.	0.03	n.d.	n.d.	0.07	n.d.	0.08	0.84	n.d.	6.7	n.d.	n.d.	0.05	0.02
w-bb-1-dup	n.d.	n.d.	n.d.	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	0.77	n.d.	5.8	n.d.	n.d.	0.02	0.02

Detection Limit : 0.01 – 0.1 ppm

n.d. : Not detected

**TABLE 4. METALS ANALYSES FOR HALIFAX SEDIMENTS SAMPLES (PPM)**

<b>SAMPLE</b>	<b>% Sediment</b>	<b>Ag</b>	<b>Al</b>	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Bi</b>	<b>Cd</b>	<b>Co</b>	<b>Cr</b>	<b>Cu</b>	<b>Fe</b>	<b>Hg</b>	<b>Mn</b>	<b>Mo</b>	<b>Ni</b>	<b>P</b>	<b>Pb</b>	<b>Sb</b>	<b>Si</b>	<b>Sn</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>
<b>s-sd-1</b>	38.1	1.1	20000	4.9	53	53	0.2	n.d.	0.2	8	28	n.d.	33000	n.d.	480	n.d.	19	530	78	1	2500	n.d.	190	35	48
<b>s-sd-2</b>	49.9	n.d.	22000	5.5	58	56	0.4	10	0.3	8.9	29	n.d.	37000	n.d.	560	n.d.	19	520	86	1	3300	2.7	280	37	49
<b>s-sd-20L</b>	45.2	n.d.	25000	5.5	61	59	0.4	n.d.	0.3	9.7	34	n.d.	40000	n.d.	660	n.d.	24	710	100	1.4	2400	4.1	210	41	69
<b>CCME ISQG</b>		N/A	N/A	7.24	N/A	N/A	N/A	N/A	0.7	N/A	N/A	18.7	N/A	0.13	N/A	N/A	N/A	N/A	30.2	N/A	N/A	N/A	N/A	N/A	124

Detection Limit : 0.1 – 6 ppm

n.d. : Not detected

N/A : Not applicable

CCME ISQG : Canadian Council of Ministers of Environment Interim Sediments Quality Guideline

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The intense maritime military activities, such as live fire training, capabilities assessment or even war, can incur damage to the environment. Numerous ships have sunk through the years in Canada's territorial waters. The ammunition stock that sank with them is likely to liberate contaminants in the aquatic environment. In this context, two separate studies were conducted, with the objective of collecting water and sediments samples in order to detect potential contamination by explosives or heavy metals. The first study was conducted at Point Amour, Labrador, where HMS Raleigh ran aground in 1922. Unexploded ordnances were present and in situ detonation was performed. Divers performed sampling before and after each detonation, along with a control site. The second study was conducted in the Halifax Harbour area, where two shipwrecks and one ammunition dumping area were considered. For this study, water and sediments sampling were performed, using a remote operation vehicle (ROV) at various spots in order to find contamination. For the Raleigh operation, trace levels of explosives were detected after detonation events. In the Halifax study, analyses showed no contamination by EM, but some high levels of metals, such as lead, were detected in sediments samples. Those two studies have demonstrated the importance of significant factors, such as sample manipulation and identification, weather conditions and sampling methods in deep water.

Les nombreuses activités maritimes militaires, telles que l'entraînement au tir réel, l'évaluation des capacités de défense ou encore la guerre, peuvent occasionner de sérieux dommages à l'environnement. Plusieurs navires ont sombré dans les eaux territoriales canadiennes au fil des ans. L'amoncellement de munitions qui a coulé avec ces navires est susceptible de libérer des contaminants dans l'environnement aquatique. Dans ce contexte, deux études différentes ont été menées, avec comme objectif de prélever des échantillons d'eau et des sédiments marins afin de détecter une contamination potentielle par les explosifs ou les métaux. La première étude a été menée à Pointe Amour, au Labrador, où le HMS Raleigh sombra en 1922. Des munitions non éclatées s'y trouvaient et on a procédé à la détonation in situ de ces munitions. Des plongeurs se sont chargés de recueillir des échantillons avant et après chaque détonation sur le site, de même que sur un site de contrôle. La deuxième étude a été effectuée à Halifax, où se trouvaient deux épaves de navires de guerre de même qu'un dépotoir de munitions. Au cours de cette opération, l'échantillonnage d'eau et de sédiments a été effectué à l'aide d'un véhicule submersible télécommandé. En ce qui concerne l'opération Raleigh, des traces d'explosifs ont été détectées dans quelques échantillons après la détonation. Pour ce qui est de l'étude menée à Halifax, les analyses n'ont montré aucune contamination par les matériaux énergétiques, mais certains métaux lourds, tels que le plomb, ont été détectés dans les échantillons de sédiments. Ces deux études ont su démontrer l'importance de facteurs significatifs, tels que la manipulation et l'identification des échantillons, les conditions météorologiques ainsi que les méthodes d'échantillonnage en eau profonde.

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